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# Enthalpy of dissociation and hydration number of carbon dioxide hydrate from the Clapeyron equation

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## Abstract

The enthalpies of the reactions in which carbon dioxide hydrate is dissociated to carbon dioxide vapor and either water or ice are determined by an analysis with the Clapeyron equation. The most important feature of the new analysis is the direct use of the Clapeyron equation rather than the Clausius-Clapeyron equation. The analysis takes into account the finite volumes of the condensed phases, the nonideality of the vapor phase, and the solubility of carbon dioxide in water. New data for the solubility in the vicinity of the (water + hydrate + vapor) coexistence curve are employed. The enthalpy change of the reaction  $\text{CO}_2 \cdot n\text{H}_2\text{O(s)} = \text{CO}_2(\text{g}) + n\text{H}_2\text{O(l)}$  is found to vary from  $(63.6 \pm 1.8) \text{ kJ} \cdot \text{mol}^{-1}$  to  $(57.7 \pm 1.8) \text{ kJ} \cdot \text{mol}^{-1}$  between quadruple points Q1 and Q2, and the hydration number varies from  $(6.6 \pm 0.3)$  to  $(5.6 \pm 0.3)$  over the same range. The results are compared to values reported in the literature that were determined by various techniques.

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**Keywords:** Carbon dioxide hydrate; Enthalpy of dissociation; Hydration number

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## 1. Introduction

Interest in the class of compounds known as gas hydrates has been increasing in recent years. Naturally occurring hydrates of methane and carbon dioxide play an

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important role in the terrestrial carbon balance. Industrial applications of carbon dioxide hydrates are being investigated as means for energy production and/or carbon sequestration. Yet despite decades or even centuries of study, the most basic properties of many hydrate compounds are not known with certainty. This is especially true for carbon dioxide hydrate, for which a large range of values have been reported for the enthalpy of dissociation and the hydration number.

This paper uses an old technique for determining the enthalpies of dissociation and hydration number for the dissociation of solid hydrate to gaseous carbon dioxide and (1) liquid water, or (2) ice. The method, which utilizes the Clapeyron equation, was first used extensively by de Forcrand [1]. The analysis must make adjustments for nonideality of the gas phase, the finite volume of the condensed phases, and for the solubility of the gas in liquid water, all significant effects for carbon dioxide. This work is an improvement on previous analyses for several reasons:

1. it uses the Clapeyron equation directly, avoiding the simplifying assumptions that must be made to use the Clausius-Clapeyron equation;
2. it utilizes a compendium of new and old high-quality hydrate phase equilibrium data; and
3. it utilizes recently published data [2] for the solubility of carbon dioxide in water in the appropriate temperature and pressure regime.

## 2. Method of analysis

The following two equations represent the dissociation of CO<sub>2</sub> hydrate to gaseous CO<sub>2</sub> and liquid water, and to gaseous CO<sub>2</sub> and ice, respectively:



Once accurate values for the enthalpy changes of reactions (I) and (II) are known, it is an easy matter to determine  $n$  since the difference between reactions (I) and (II) represents the melting of  $n$  moles of ice, whose enthalpy change per mole is well known  $\{\Delta_s^1 H(\text{H}_2\text{O}) = 6.01 \text{ kJ} \cdot \text{mol}^{-1}\}$ :



where

$$\Delta H_{\text{III}} = \Delta H_{\text{I}} - \Delta H_{\text{II}} = n\Delta_s^1 H(\text{H}_2\text{O}). \quad (1)$$

Strictly speaking, equation (1) is only valid at the quadruple point Q1, where both reactions (I) and (II) occur simultaneously. If one wanted to use equation (1) to calculate the hydration number at temperatures above Q1, the value of  $\Delta H_{\text{I}}$  would have to be corrected to the equivalent value that it would have at Q1. For carbon dioxide hydrate, however, the pressure and temperature range of the (liquid, hydrate, vapor) region is modest, such that the temperature and pressure corrections to  $\Delta H_{\text{I}}$  are smaller than the experimental error in  $\Delta H_{\text{I}}$ . An attractive feature of the

Clapeyron equation as applied to reactions (I) and (II) is that it gives the enthalpy change per mole of  $\text{CO}_2$  in the hydrate; in principle it is not necessary to know  $n$  in advance. Due to slight complications caused by the solubility of  $\text{CO}_2$  in water, however, it is necessary in practice to know an approximate value of  $n$ . A more accurate value of  $n$  is then determined by iteration.

The validity of the Clapeyron equation depends on the fact that the chemical equilibrium in either of reactions (I) or (II) is univariant. Univariance is evident from the phase rule.

The Clapeyron equation relates the differential pressure change  $dp$  that accompanies a differential temperature change  $dT$  in a system where two or more phases are in equilibrium. We present it without derivation as

$$\frac{dp}{dT} = \frac{\Delta S}{\Delta V} = \frac{\Delta H}{T\Delta V}, \quad (2)$$

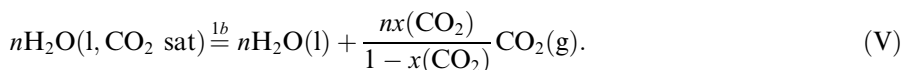
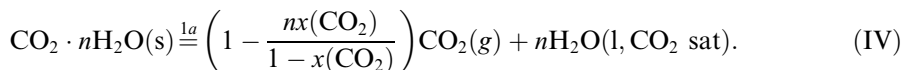
where  $\Delta S$ ,  $\Delta H$  and  $\Delta V$  are the entropy, enthalpy and volume changes that take place due to the phase change. Solving for  $\Delta H$  gives

$$\Delta H = T\Delta V(dp/dT). \quad (3)$$

In most previous analyses [3–5] using the Clapeyron equation, simplifying assumptions are made at this point and equation (3) is transformed into the Clausius-Clapeyron equation. Some of the assumptions can be shown to lead to inaccuracy; we prefer to work directly with equation (3). Starting from the  $(p, T)$  data for the three phase equilibrium and the equation of state of the vapor phase, we proceed as follows: select  $T$ ; determine  $p$  from the data; determine  $dp/dT$  from the data; find  $\Delta V(p, T)$  (see below); and calculate  $\Delta H$  from equation (3).

### 2.1. Method for determining the enthalpy of dissociation of hydrate to $\text{CO}_2$ vapor and ( $\text{CO}_2$ saturated) liquid water

Reaction (I) is an idealization in that the water is in the pure liquid state, whereas the water actually in equilibrium with the hydrate is saturated with respect to  $\text{CO}_2$ . Suppose that the mole fraction of  $\text{CO}_2$  in the water in equilibrium with the hydrate is  $x(\text{CO}_2)$ . When 1 mol of hydrate decomposes,  $n$  moles of water are formed, which contain  $nx(\text{CO}_2)/\{1 - x(\text{CO}_2)\}$  moles of dissolved  $\text{CO}_2$ . Thus reaction (I) must be analyzed as the sum of the following two reactions;



The designation  $\text{H}_2\text{O(l, CO}_2 \text{ sat)}$  refers to liquid water that is saturated with respect to  $\text{CO}_2$  at the given temperature and pressure. The enthalpy change of reaction (IV) is found from the Clapeyron equation, while the enthalpy change of reaction (V) is found from the enthalpy of solution of carbon dioxide in water.

## 2.2. Finding $dp/dT$

The  $(p, T)$  data are fitted to an analytical function, which is then differentiated to find  $(dp/dT)$ . The fitting function need not have any theoretical significance; it is sufficient that it represents the data well over the entire range of temperature and may be conveniently differentiated. Polynomial fitting functions are used in this work. The process is necessarily somewhat subjective; a low-order fitting function may fail to represent the data whereas a high-order function may introduce artifacts which become significant when the function is differentiated.

Most of the data for the (liquid, hydrate, vapor) coexistence line used in this work were taken from tables given by Sloan [6], who compiled data from several sources. The data sets that were used in this work are from Deaton and Frost [7], Unruh and Katz [8], Robinson and Mehta [9], Ng and Robinson [10], Vlahakis *et al.* [5], and Adisasmito, *et al.* [11]. One source in Sloan that was *not* used was the data set of Larson [3], since his data appeared to deviate very slightly but systematically from all of the other data sets. Also used was a set of data from Wendland *et al.* [12] that appeared after Sloan's publication. The “complete” set of data (73 points in all) are shown in figure 1, along with a fifth-order polynomial fit.

The actual fitting process used the Celsius temperature  $t/^\circ\text{C} = T/\text{K} - 273.15$ . This offset results in smaller absolute values for the fit coefficients and allows the function to be calculated using fewer significant digits. The fifth-order polynomial was the lowest order that adequately fitted the data. The functions  $p(T)$  and  $(dp/dT)$  are expressed as follows;

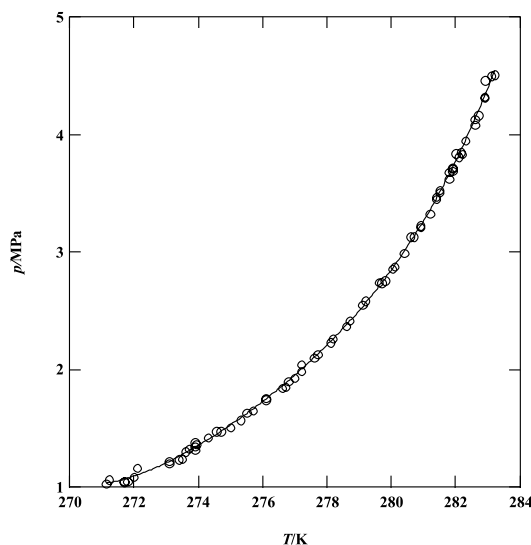


FIGURE 1.  $(p, T)$  data along the (liquid, hydrate, vapor) coexistence line for  $\text{CO}_2$  hydrate, with superimposed fifth-order polynomial fit.

TABLE 1  
Fitting parameters for equations (6) and (7)

$a_0$	1.2241
$a_1$	0.13700
$a_2$	0.016771
$a_3$	-0.0015018
$a_4$	0.0001733

$$p^{\text{LHV}}/\text{MPa} = a_0 + a_1(T/\text{K} - 273.15) + a_2(T/\text{K} - 273.15)^2 + a_3(T/\text{K} - 273.15)^3 + a_4(T/\text{K} - 273.15)^4, \quad (4)$$

$$\frac{d(p^{\text{LHV}}/\text{MPa})}{d(T/\text{K})} = a_1 + 2a_2(T/\text{K} - 273.15) + 3a_3(T/\text{K} - 273.15)^2 + 4a_4(T/\text{K} - 273.15)^3. \quad (5)$$

The superscript LHV is used to identify the three phases (liquid, hydrate, vapor) in equilibrium. Table 1 gives the fitting parameters.

### 2.3. Finding $\Delta V(p, T)$

The volume change for reaction (IV) is

$$\Delta V = \left(1 - \frac{nx(\text{CO}_2)}{1 - x(\text{CO}_2)}\right) V_{\text{vapor}} + nV_{\text{liquid}} - V_{\text{hyd}}. \quad (6)$$

We need expressions for the volumes of hydrate (1 mol), liquid (containing  $n$  moles of water), and vapor in order to evaluate equation (8). The term  $V_{\text{vapor}}$  refers to the molar volume of pure  $\text{CO}_2$  vapor at  $T$ ,  $p$ . This is because the vapor contains a negligible amount of water.  $V(\text{CO}_2)$  was found at each  $T$ ,  $p$  using the carbon dioxide equation of state in the NIST WebBook [13].

The molar volume of the hydrate comes from a recent X-ray diffraction study of Udachin *et al.* [14] in which the density of hydrate formed at  $T = 276$  K was found to be  $1120 \text{ kg} \cdot \text{m}^{-3}$ . Anticipating that the hydration number will be about 6.2, the hydrate molecular weight is approximately  $0.044 + 6.2(0.018) = 0.1556 \text{ kg} \cdot \text{mol}^{-1}$ . Thus  $V_{\text{hyd}} \approx 1.389 \cdot 10^{-4} \text{ m}^3 \cdot \text{mol}^{-1}$ . Small changes in  $n$  will have a negligible effect on this value as far as subsequent calculations are concerned.  $V_{\text{hyd}}$  can also be shown to vary insignificantly with temperature and pressure.

The molar volume of the liquid is the sum of contributions from  $\text{CO}_2$  and  $\text{H}_2\text{O}$ .

$$V_{\text{liquid}} = x(\text{CO}_2)V(\text{CO}_2, \text{H}_2\text{O}) + \{1 - x(\text{CO}_2)\}V(\text{H}_2\text{O}, \text{CO}_2). \quad (7)$$

For the partial molar volumes we use the infinite dilution values since  $x(\text{CO}_2)$  is quite small. The author [2] recently determined  $V^\infty(\text{CO}_2, \text{H}_2\text{O}) = 3.84 \cdot 10^{-5} \text{ m}^3 \cdot \text{mol}^{-1}$ , in good agreement with other measurements in the literature. The molar volume of water is  $V(\text{H}_2\text{O}) = 1.80 \cdot 10^{-5} \text{ m}^3 \cdot \text{mol}^{-1}$ . Substituting into equation (7),

$$V_{\text{liquid}}/(\text{m}^3 \cdot \text{mol}^{-1}) = \{1.8 \cdot 10^{-5} + 2.04 \cdot 10^{-5}x(\text{CO}_2)\}. \quad (8)$$

Substituting into equation (6),

$$\Delta V/(\text{m}^3 \cdot \text{mol}^{-1}) = \left(1 - \frac{nx(\text{CO}_2)}{1 - x(\text{CO}_2)}\right)V(\text{CO}_2)/(\text{m}^3 \cdot \text{mol}^{-1}) + n\{1.8 \cdot 10^{-5} + 2.04 \cdot 10^{-5}x(\text{CO}_2)\} - 1.389 \cdot 10^{-4}. \quad (9)$$

Substituting equation (9) into equation (3), we find an expression for the enthalpy change of reaction (IV).

$$\Delta H_{1a}/(\text{J} \cdot \text{mol}^{-1}) = 10^6 \cdot (T/\text{K}) \cdot \{(dp/dT)/(\text{MPa} \cdot \text{K}^{-1})\} \cdot \left\{ \left(1 - \frac{nx(\text{CO}_2)}{1 - x(\text{CO}_2)}\right)V(\text{CO}_2)/(\text{m}^3 \cdot \text{mol}^{-1}) + n(1.8 \cdot 10^{-5} + 2.04 \cdot 10^{-5}x(\text{CO}_2)) - 1.389 \cdot 10^{-4} \right\}. \quad (10)$$

Reaction (V) represents (in reverse) the formation of a saturated solution of  $\text{CO}_2$  in water, at a pressure corresponding to the (liquid, hydrate, vapor) phase boundary at a given temperature. The reaction is nonstoichiometric;  $x(\text{CO}_2)$  varies with temperature and pressure and therefore so does the enthalpy change due to reaction. However, the solubility of  $\text{CO}_2$  in water is low, such that the mole fraction  $x(\text{CO}_2)$  does not exceed 0.03 in the hydrate-forming region. Therefore, the enthalpy of solution at *infinite dilution* for  $\text{CO}_2$  in water can be used with little error. This value ( $\Delta H^\infty(\text{CO}_2, \text{H}_2\text{O}) = -22.83 \text{ kJ} \cdot \text{mol}^{-1}$ ) has been determined from recent measurements [2] by the author of the Henry's law constants *versus* temperature.

$$\Delta H_{1b}/(\text{J} \cdot \text{mol}^{-1}) = \frac{22,830nx(\text{CO}_2)}{1 - x(\text{CO}_2)}. \quad (11)$$

Combining equations (10) and (11), we arrive at an equation for the enthalpy change of reaction 1. This result contains more refinements than have been applied to the analysis of gas hydrates in any previous work. These are the use of the Clapeyron equation directly, real gas effects in the vapor phase, finite volumes of water and hydrate phase, and treatment of gas solubility in water. Each of these effects is significant in the formation of  $\text{CO}_2$  hydrate.

#### 2.4. Error analysis for the determination of $\Delta H_1$

The uncertainty in the determination of  $\Delta H_1$  is dominated by the error limits associated with finding  $dp/dT$ . To estimate this quantity, small regions of the  $(p, T)$  data space were linearly fitted as  $\ln(p)$  *versus*  $1/T$ , which resulted in apparently straight lines if a small enough temperature interval was chosen. The standard deviations in the slopes of these "local" fits were used to estimate the slope uncertainty. The standard deviation of  $dp/dT$  was about 1.5 per cent between  $T = 274.15 \text{ K}$  and  $T = 280.15 \text{ K}$ , and increased to about 3 per cent at  $T = 282.15 \text{ K}$ . Using  $\pm 2\sigma$  as a fairly conservative error limit, we estimate that our individual determinations of

$\Delta H_1$  are accurate to  $\pm 3$  per cent from  $T = 274.15$  K to  $T = 280.15$  K, with the error increasing to  $\pm 6$  per cent at  $T = 282.15$  K. Below  $T = 274.15$  K and above  $T = 282.15$  K, the uncertainty becomes much greater. At the low temperature end this is probably due to experimental difficulties in the  $(p, T)$  measurements; it is very difficult to form hydrates near the ice point while assuring that no ice phase is present. At the high temperature end the large uncertainty in  $dp/dT$  is believed to be a numerical artifact; slope determination near the ends of the range of a fitting function is unreliable. For this reason the data below  $T = 274.15$  K and above  $T = 282.15$  K were not used in the determination of  $\Delta H_1$ .

### 2.5. Method for determining the enthalpy of dissociation of hydrate to $\text{CO}_2$ vapor and ice (reaction (II))

The use of the Clapeyron equation to determine  $\Delta H_2$  is much simpler than the analysis for  $\Delta H_1$ . The reasons are that (1), the volume difference between ice and hydrate is almost negligible with respect to the volume of the vapor phase, and (2)  $\text{CO}_2$  is almost insoluble in ice. Thus equation (3) is used directly, with  $\Delta V = V(\text{CO}_2)$ .

The only extensive  $p$ - $T$  data set for the {ice + hydrate + vapor (I + H + V)} coexistence line is that of Larson [3]. His data are plotted in figure 2. A third-order polynomial fit is superimposed on the data. As before, we fit to the Celsius temperature.

Expressions for  $p$  and  $dp/dT$  are given below. The fitting parameters are given in table 2.

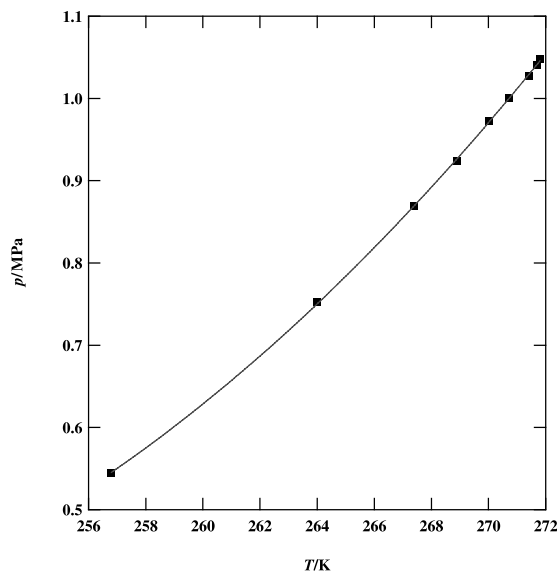


FIGURE 2.  $(p, T)$  along the (ice, hydrate, vapor) coexistence line for  $\text{CO}_2$  hydrate. ■, data of Larson [3]; —, third-order polynomial fit.

TABLE 2

Fitting parameters for equations (14) and (15)

$b_0$	1.1046
$b_1$	0.04449
$b_2$	0.000629

$$p^{\text{IHV}}/\text{MPa} = b_0 + b_1(T/\text{K} - 273.15) + b_2(T/\text{K} - 273.15)^2. \quad (12)$$

$$\frac{dp^{\text{IHV}}/\text{MPa}}{dT/\text{K}} = b_1 + 2b_2(T/\text{K} - 273.15). \quad (13)$$

### 3. Results

The analysis was done according to the following outline:

1. estimate the hydration number  $n$  (first guess  $n = 6.0$ );
2. find estimates for  $\Delta H_{\text{I}}$  and  $\Delta H_{\text{II}}$ ;
3. solve for  $n$  from  $n = \{(\Delta H_{\text{I}} - \Delta H_{\text{II}})/(\text{kJ} \cdot \text{mol}^{-1})\}/6.01$ ; and
4. iterate if necessary until the apparent value of  $n$  is constant.

The results for  $(\Delta H_{\text{I}}, n)$  and for  $\Delta H_{\text{II}}$  are given in tables 3 and 4.

The mean value of  $\Delta H_{\text{II}}$  is  $(23.77 \pm 0.40) \text{ kJ} \cdot \text{mol}^{-1}$  and there is almost no variation with temperature. The error limits are set at  $\pm 2$  times the standard deviation of the mean. The behavior of  $\Delta H_{\text{I}}$  as a function of temperature is plotted in figure 3.

A straight line fit through the data in figure 3 gives the following result;

$$\Delta H_{\text{I}}/(\text{kJ} \cdot \text{mol}^{-1}) = \{62.9 - 0.53(T/\text{K} - 273.15)\} \pm 1.8. \quad (14)$$

Combining equations (1) and (14) along with  $\Delta H_{\text{II}} = (23.77 \pm 0.40) \text{ kJ} \cdot \text{mol}^{-1}$  gives the following relation for the hydration number;

$$n = \{6.51 - 0.088(T/\text{K} - 273.15)\} \pm 0.3. \quad (15)$$

At quadruple point Q1 ( $T = 271.8 \text{ K}$ ),

$$\Delta H_{\text{I}}(Q1) = (63.6 \pm 1.8) \text{ kJ} \cdot \text{mol}^{-1}, \quad n(Q1) = 6.6 \pm 0.3. \quad (16)$$

At quadruple point Q2 ( $T = 283.1 \text{ K}$ ),

$$\Delta H_{\text{I}}(Q2) = (57.6 \pm 1.8) \text{ kJ} \cdot \text{mol}^{-1}, \quad n(Q2) = 5.6 \pm 0.3. \quad (17)$$

### 4. Discussion

To date only two experimental techniques have been developed to determine  $\Delta H_{\text{I}}$ ; they are the present method using the Clapeyron equation and the calorimetric method. These techniques yield a value for the hydration number as well. Numerous additional techniques have been used to independently measure or infer the hydration number. These results are summarized in table 5.



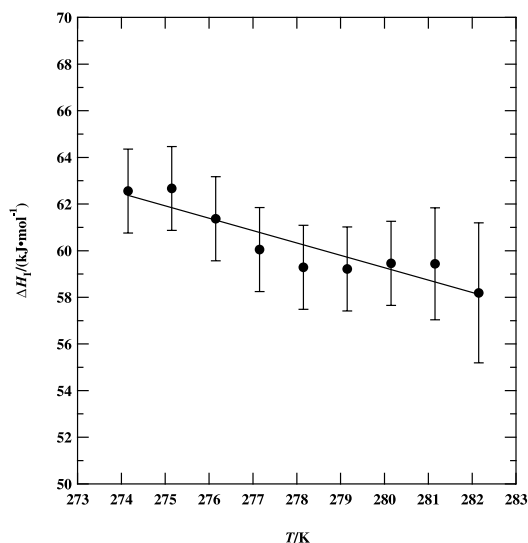
TABLE 3  
Enthalpy change  $\Delta H$  and hydration number  $n$  for reaction (I) and temperature  $T$  and pressure  $p$  for mole fraction  $x$  of  $\text{CO}_2$

$T/\text{K}$	$p/\text{MPa}$	$(dp/dT)$ ( $\text{MPa} \cdot \text{K}^{-1}$ )	$x(\text{CO}_2)$	$\Delta H_{\text{IV}}$ ( $\text{kJ} \cdot \text{mol}^{-1}$ )	$\Delta H_{\text{V}}$ ( $\text{kJ} \cdot \text{mol}^{-1}$ )	$\Delta H_{\text{I}}$ ( $\text{kJ} \cdot \text{mol}^{-1}$ )	$n$
274.15	1.377	$0.167 \pm 0.005$	0.0162	$60.1 \pm 1.8$	2.42	$62.5 \pm 1.8$	$6.4 \pm 0.3$
275.15	1.556	$0.192 \pm 0.006$	0.0174	$60.1 \pm 1.8$	2.60	$62.7 \pm 1.8$	$6.5 \pm 0.3$
276.15	1.760	$0.216 \pm 0.006$	0.0187	$58.7 \pm 1.8$	2.71	$61.4 \pm 1.8$	$6.2 \pm 0.3$
277.15	1.989	$0.243 \pm 0.007$	0.0200	$57.3 \pm 1.8$	2.80	$60.0 \pm 1.8$	$6.0 \pm 0.3$
278.15	2.249	$0.279 \pm 0.008$	0.0214	$56.4 \pm 1.8$	2.94	$59.3 \pm 1.8$	$5.9 \pm 0.3$
279.15	2.550	$0.326 \pm 0.010$	0.0228	$56.1 \pm 1.8$	3.13	$59.2 \pm 1.8$	$5.9 \pm 0.3$
280.15	2.906	$0.389 \pm 0.011$	0.0244	$56.1 \pm 1.8$	3.38	$59.5 \pm 1.8$	$5.9 \pm 0.3$
281.15	3.335	$0.472 \pm 0.021$	0.0261	$55.8 \pm 2.4$	3.62	$59.4 \pm 2.4$	$5.9 \pm 0.3$
282.15	3.858	$0.579 \pm 0.035$	0.0279	$54.5 \pm 3.0$	3.74	$58.2 \pm 3.0$	$5.7 \pm 0.3$

TABLE 4

Enthalpy change  $\Delta H$  for reaction (II) at temperature  $T$  and pressure  $p$ 

$T/\text{K}$	$p/\text{MPa}$	$\frac{dp}{dT}$ ( $\text{MPa} \cdot \text{K}^{-1}$ )	$V(\text{CO}_2)$ ( $\text{m}^3 \cdot \text{mol}^{-1}$ )	$\Delta H_{\text{II}}$ ( $\text{kJ} \cdot \text{mol}^{-1}$ )
259.15	0.605	0.2688	3.385	23.58
260.15	0.632	0.2814	3.245	23.75
261.15	0.661	0.2940	3.110	23.87
262.15	0.691	0.3065	2.980	23.95
263.15	0.723	0.3191	2.856	23.99
264.15	0.755	0.3317	2.738	23.99
265.15	0.789	0.3443	2.625	23.96
266.15	0.824	0.3568	2.518	23.91
267.15	0.860	0.3694	2.415	23.83
268.15	0.898	0.3820	2.317	23.74
269.15	0.937	0.3946	2.224	23.62
270.15	0.977	0.4071	2.136	23.50
271.15	1.018	0.4197	2.052	23.36

FIGURE 3. Enthalpy of dissociation  $\Delta H$  of  $\text{CO}_2$  hydrate to  $\text{CO}_2$  vapor and liquid water using the Clausius-Clapeyron equation.

The first thing to note about table 5 is that in most cases there is a *single* entry for  $\Delta H_I$  and/or  $n$ . In some cases the measurement technique only gives a value at a single point. In other cases there is an a priori assumption that  $\Delta H_I$  and  $n$  are constant, and thus the analysis gives an average value. This is particularly true of the previous analyses using the Clausius-Clapeyron equation. The small temperature variation in  $\Delta H_I$  found by Bozzo *et al.* [4] came from a minor correction term only; they also missed the larger variation in  $\Delta H_I$  that is seen in the present study.

TABLE 5

Reported values of the enthalpy of dissociation  $\Delta H_1$  and/or hydration number  $n$  for carbon dioxide hydrate

Reference	Technique	$\Delta H_1$	$n$
		(kJ · mol <sup>-1</sup> )	
Larson [3]	Clausius-Clapeyron equation	60.2	6.07
Bozzo <i>et al.</i> [4]	Clausius-Clapeyron equation	58.99 at 0 °C	7.30
		58.16 at 10 °C	
Vlahakis <i>et al.</i> [5]	Clausius-Clapeyron equation	59.9	
Long [15]	Clausius-Clapeyron equation	73	
Kamath [16]	Clausius-Clapeyron equation	80.1	
Yoon <i>et al.</i> [17]	Clausius-Clapeyron equation	57.66 at Q1	6.21
This work	Clapeyron equation	63.6 at Q1	6.6 ± 0.3
		57.6 at Q2	5.6 ± 0.3
Kang <i>et al.</i> [18]	Calorimetry	65.22 ± 1.03	7.23
Udachin <i>et al.</i> [14]	X-ray diffraction		6.20 ± 0.15
Vlahakis <i>et al.</i> [5]	Miller and Strong		7.30 ± 0.13
Uchida <i>et al.</i> [19]	Raman		7.24 to 7.68
Ripmeester and Ratcliffe [20]	NMR		≥ 7.0
Aya <i>et al.</i> [21]	Pressure drop		6 to 7.8

In a review Uchida [22] points out that techniques which attempt to measure the hydration number directly (*e.g.*, the last six entries in table 5) suffer from many problems concerning sample preparation and assumptions made in analysis. When it is also considered that  $n$  apparently depends on the conditions under which the hydrates were formed, it is not surprising that there is a large scatter in the measured values. It is notable, however, that Udachin *et al.* [14], using X-ray diffraction, determine  $n = 6.20$  for a hydrate crystal that was grown at  $T = 276$  K. The present work predicts  $n = (6.23 \pm 0.3)$  at that temperature.

Theoretical considerations allow a wide range of variation in the hydration number. If all of the cages in a SI hydrate structure are filled, the hydration number is  $n = 46/8 = 5.75$ . If however, only the large cages are filled, the hydration number is  $n = 46/6 = 7.67$ . The size of the CO<sub>2</sub> molecule is very close to the size of the SI small cage, making it uncertain how well it can fit. Sum *et al.* [23] using Raman spectroscopy, found no evidence for CO<sub>2</sub> in the small cages in a mixed CH<sub>4</sub>/CO<sub>2</sub> hydrate. On the other hand, Fleyfel and Devlin [24] using IR spectroscopy, and Ripmeester and Ratcliffe [20] using NMR, did see signals that they claimed were due to CO<sub>2</sub> in small cages in pure CO<sub>2</sub> hydrate. Unfortunately neither of the previous two studies was able to quantify the occupancy of the small cages. The present study implies that most or all cages are filled at  $T = 283$  K ( $n = 5.6 \pm 0.3$ ), while at  $T = 272$  K ( $n = 6.6 \pm 0.3$ ), only about half of the small cages (and all of the large cages) are filled. Since the pressure of the vapor above the hydrate at  $T = 283$  K is more than four times the pressure at  $T = 272$  K, it is not surprising that higher occupancy of the cages is favored at the higher temperature.

Previous determinations of  $\Delta H_1$  using the Clausius-Clapeyron equation have yielded varying results. Some of the reasons have been addressed earlier in this work.

The results of Long [15] and Kamath [16] are unreasonably large in magnitude. Our results agree most closely with those of Larson [3] and Vlahakis *et al.* [5] whose values  $\{(60.2 \text{ and } 59.9) \text{ kJ} \cdot \text{mol}^{-1}, \text{ respectively}\}$ , are very close to the average  $(60.6 \pm 1.8) \text{ kJ} \cdot \text{mol}^{-1}$  of our values at Q1 and Q2. We disagree with Bozzo *et al.* [4] about the temperature variation, but their average value of  $\Delta H_1 = 58.8 \text{ kJ} \cdot \text{mol}^{-1}$  agrees with our average within experimental error. Yoon *et al.* [17] correctly noted the various erroneous assumptions that are often made in using the Clausius-Clapeyron equation for gas hydrates. They give approximate ranges for the errors that can arrive from each of the assumptions. They derive an elaborate corrected form of the Clausius-Clapeyron equation, from which they arrive at a value of  $\Delta H_1 = 57.66 \text{ kJ} \cdot \text{mol}^{-1}$ . They do not provide enough details to evaluate their results, nor do they quote uncertainties. Also, it is unclear why “fixing” the Clausius-Clapeyron equation is preferable to using the simple and rigorous Clapeyron equation directly. Kang *et al.* [18], using a calorimetric technique, report a value of  $\Delta H_1 = (65.22 \pm 1.03) \text{ kJ} \cdot \text{mol}^{-1}$  for a hydrate sample that was prepared at  $T = 278.15 \text{ K}$ , in poor agreement with our value of  $(60.25 \pm 1.90) \text{ kJ} \cdot \text{mol}^{-1}$  at that temperature. Calorimetric measurements are usually preferred over the Clapeyron analysis technique since calorimetry is more “direct.” However, in the same work Kang *et al.* [18] report a value for the enthalpy of dissociation of methane hydrate  $(56.84 \pm 0.89) \text{ kJ} \cdot \text{mol}^{-1}$  that differs from that reported for methane hydrate by Handa [25]  $(54.19 \pm 0.28) \text{ kJ} \cdot \text{mol}^{-1}$  using a similar calorimetric technique. The difference in the Kang and Handa results is much greater than would be expected based on their stated precision, indicating that systematic errors could have been present in one or both of the calorimetric measurements. Sloan [26] reports that for hydrates of methane, ethane, propane, and isobutane, which have been measured by both techniques, the calorimetric results of Handa [25] agree within  $3 \text{ kJ} \cdot \text{mol}^{-1}$  with the results using the Clapeyron equation. Thus both techniques for the determination of  $\Delta H_1$  give consistent results but it is not clear which is most accurate.

## 5. Conclusions

The present study unfortunately does not completely resolve the controversy about the enthalpy of dissociation and the hydration number of carbon dioxide hydrate. Our results suggest, however, that the hydrate stoichiometry depends on the conditions of formation, and that this fact alone could account for much of the scatter in the reported values of  $\Delta H_1$  and  $n$ . Our range of values for the hydration number  $\{(5.6 \text{ to } 6.6) \pm 0.3\}$  is consistent with the idea that complete occupancy of the small cages in the SI structure can only occur at sufficiently high pressure. We argue that the technique employing the Clapeyron equation directly is preferred to the use of the Clausius-Clapeyron equation for determining the enthalpy of dissociation of hydrates. Even when calorimetric results are available, their apparently higher precision should not be taken at face value unless systematic errors have been rigorously ruled out.

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